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⑰ **Process and catalyst for polyolefin density and molecular weight control.**

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DIE MAKROMOLEKULARE CHEMIE, vol. 182,
no. 4, April 16, 1981 HEIDELBERG (DE) J.
CIHLÄR et al.: "Polymerization of Ethylene
Catalyzed by Titanocene Systems, 2a, Catalytic
Systems CP2 TiRCl/Oxyaluminium
Compounds", pages 1127-1134

The file contains technical information
submitted after the application was filed and
not included in this specification

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Comprehensive organometallic chemistry, 8,
page 1058 (Pergamon Press; Sir G. Wilkinson,
Editor)
Journal of Polymer Science, 55, pages 145-152
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Die Makromolekulare Chemie, 148, 107-118
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Description

This invention relates to catalyst suitable for the polymerisation of an olefin.

The catalyst can be used in an improved process for polymerising olefins and more particularly in a method of controlling the molecular weight and/or the density of polyolefins produced so as to obtain polymer product in any desired range of molecular weight and densities. The invention particularly relates to the polymerisation of ethylene in the presence or absence of comonomers to polyethylenes of controlled molecular weight and density.

In US Patent 3,051,690 of Vandenberg, there is described a process of polymerising olefins to high molecular weight polyolefins of controlled molecular weight, as indicated by polymer viscosity, by the addition of controlled amounts of hydrogen to the polymerisation system. The molecular weight control was described as useful in combination with a hydrocarbon insoluble catalyst system comprising the reaction product of a compound of a metal of Group IVB, VB, VIB, and VIII with an organometallic compound of an alkali metal, alkaline earth metal, zinc, earth metal or rare earth metal. The patent teaches that increased use of hydrogen during the polymerisation process results in the decrease of polymer product viscosity.

It is further known that certain metallocenes such as bis(cyclopentadienyl) titanium or zirconium dialkyls in combination with aluminium alkyl/water cocatalyst form homogeneous catalyst systems for the polymerisation of ethylene.

German Patent Application 2,608,863 discloses the use of a catalyst system for the polymerization of ethylene consisting of bis (cyclopentadienyl) titanium dialkyl, aluminum trialkyl and water.

German Patent Application 2,608,933 discloses an ethylene polymerization catalyst system consisting of zirconium metallocenes of the general formula $(\text{cyclopentadienyl})_n\text{ZrY}_{4-n}$, wherein n stands for a number in the range of 1 to 4, Y for R, CH_2AIR_2 , $\text{CH}_2\text{CH}_2\text{AIR}_2$ and $\text{CH}_2\text{CH}(\text{AIR}_2)_2$, wherein R stands for alkyl or metallo alkyl, an aluminum trialkyl cocatalyst and water.

European Patent Appln. No. 0035242 discloses a process for preparing ethylene and atactic propylene polymers in the presence of a halogen-free Ziegler catalyst system of (1) cyclopentadienyl compound of the formula $(\text{cyclopentadienyl})_n\text{MeY}_{4-n}$ in which n is an integer from 1 to 4, Me is a transition metal, especially zirconium, and Y is either hydrogen, a C_1-C_5 alkyl or metallo alkyl group or a radical having the following general formula CH_2AIR_2 , $\text{CH}_2\text{CH}_2\text{AIR}_2$ and $\text{CH}_2\text{CH}(\text{AIR}_2)_2$ in which R represents a C_1-C_5 alkyl or metallo alkyl group, and (2) an alumoxane.

The above patents disclose that the polymerization process employing the homogeneous catalyst system is also hydrogen sensitive for molecular weight control.

An advantage of the cyclopentadienyl-metal/alumoxane catalyst system, is their extremely high activity for ethylene polymerization. Another significant advantage is that unlike olefin polymers produced in the presence of conventional heterogeneous Ziegler catalyst, terminal unsaturation is present in polymers produced in the presence of these homogeneous catalysts. The use of hydrogen for molecular weight control for these homogeneous catalysts would be disadvantageous since the terminal unsaturation would become saturated and hence, the loss of available sites for building functionalities into the olefin polymers.

In EP 35242, the patentee discloses that relatively low molecular weight polymer products are obtained at higher polymerization temperatures and relatively high molecular weight polymers at low polymerization temperatures.

As is generally known in the art, it is desirable to maximize polymerization temperatures in order to achieve high polymerization activity and reduce operating costs in terms of energy recovery. The catalyst disclosed in EP 35242 has certain disadvantages for the production of high molecular weight, high density resins since to produce such polymer products, one must operate at low temperatures thereby increasing operating costs and decreasing catalytic activity.

It would be highly desirable to provide homogeneous catalysts which can be usefully employed to produce high molecular weight polymer products at conventional polymerization temperatures and to be able to control molecular weight and density of the polymer product without resorting to temperature control or hydrogen.

Accordingly, the present invention provides new cyclopentadienyl - metal/alumoxane catalysts for olefin polymerization which catalyst can be usefully employed at high temperatures to obtain olefin polymer products having excellent properties with respect to molecular weight, density and terminal unsaturation.

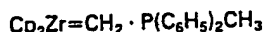
It has been discovered that the molecular weight of polymer product can be controlled by the judicious selection of the substituent on the cyclopentadienyl ring and use of ligands for the metallocenes. It has further been discovered that comonomer content can be controlled by the judicious selection of metallocenes. Hence, by the selection of catalyst components one can tailor polymer product with respect to molecular weight and density.

The catalysts usefully employed for the polymerization of ethylene and alpha-olefins to polyethylene homopolyolefins and copolyethylene- alpha-olefin comprise new metallocenes in combination with alumoxanes. The metallocenes employed in accordance with this invention are organometallic coordination compounds which are cyclopentadienyl derivatives of a Group 4b, 5b and 6b metal of the

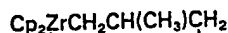
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Periodic Table and include mono, di and tricyclopentadienyl and their derivatives of the transition metals. The metallocenes include those represented by the general formula $(C_5R'_m)_pR''_n(C_5R'_m)_pMeQ_{3-p}$ or $R''_n(C_5R'_m)_2MeQ'$ wherein Me is a Group 4b, 5b, or 6b metal of the Periodic Table (Chemical Rubber Company's Handbook of Chemistry & Physics, 48th edition), $(C_5R'_m)$ is a cyclopentadienyl or substituted cyclopentadienyl, each R' , which can be the same or different, is hydrogen or a hydrocarbyl radical such as alkyl, alkenyl, aryl, alkylaryl, or arylalkyl radical having from 1 to 20 carbon atoms or two carbon atoms are joined together to form a C_4-C_6 ring, R'' is a C_1-C_4 alkylene radical, a dialkyl germanium or silicone, or a alkyl phosphine or amine radical bridging two $(C_5R'_m)$ rings, Q is a hydrocarbon radical such as aryl, alkyl, alkenyl, alkylaryl, or arylalkyl radical having from 1 to 20 carbon atoms or halogen and can be the same or different, Q' is an alkylidene radical having from 1 to 20 carbon atoms, s is 0 or 1, p is 0, 1 or 2; provided that s is 0 when p is 0; m is 4 when s is 1 and m is 5 when s is 0 and that at least one R' is a hydrocarbyl radical when s=0 and Q is an alkyl radical or halogen.

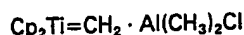
As an alternative to the above defined metallocenes one can use certain carbenes. These are the carbene represented by the formula



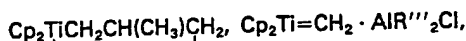
and its derivative of the formula



and the carbene represented by the formula



and the derivatives of this carbene



wherein Cp is a cyclopentadienyl or substituted cyclopentadienyl radical, and R'''' is an alkyl, aryl or alkylaryl radical having from 1—18 carbon atoms.

The molecular weight of the polymer product can be further controlled by the ratio of alumoxane to metallocene or defined carbene.

The present invention also provides a process for producing polyethylenes having molecular weight at relatively high temperatures. The process comprises polymerizing ethylene alone or in the presence of minor amounts of higher alpha-olefins or diolefins in the presence of the catalyst system described above.

The advantages of this invention are obtained by the use of derivatives of the cyclopentadienyl ring and/or other ligands for the metallocenes in order to control and tailor polymer molecular weight and/or comonomer content.

The present invention is directed towards catalyst systems and a catalytic process for the polymerization of olefins, and particularly ethylene to high molecular weight polyethylenes such as linear low density polyethylene (LLDPE) and high density polyethylene (HDPE). The polymers are intended for fabrication into articles by extrusion, injection molding, thermoforming, rotational molding, and the like. In particular, the polymers of this invention are homopolymers of ethylene, and copolymers of ethylene with higher alpha-olefins having from 3 to 10 carbon atoms and preferably 4 to 8 carbon atoms per molecule. Illustrative of the higher alpha-olefins are butene-1, hexene-1 and octene-1.

In the process of the present invention, ethylene, either alone or together with alpha-olefins having 3 or more carbon atoms per molecule, is polymerized in the presence of a catalyst system comprising at least one metallocene or carbene as hereinbefore defined and an alumoxane.

In accordance with this invention, one can also produce olefin copolymers particularly copolymers of ethylene and higher alpha-olefins having from 3—18 carbon atoms per molecule. As indicated above, the comonomer content can be controlled through the selection of metallocene or carbene catalyst component.

The alumoxanes are polymeric aluminum compounds which can be represented by the general formulae $(R-Al-O)_n$ which is a cyclic compound and $R(R-Al-O)_nAlR_2$, which is a linear compound. In the general formula R is a C_1-C_5 alkyl group such as, for example, methyl, ethyl, propyl, butyl and pentyl and n is an integer from 1 to 20. Most preferably, R is methyl. Generally, in the preparation of alumoxanes from, for example, aluminum trimethyl and water, a mixture of the linear and cyclic compounds is obtained.

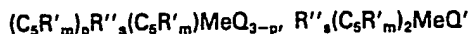
The alumoxanes can be prepared in various ways. Preferably, they are prepared by contacting water with a solution of aluminum trialkyl, such as, for example, aluminum trimethyl, in a suitable organic solvent such as benzene or an aliphatic hydrocarbon. For example, the aluminum alkyl is treated with water in the

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form of a moist solvent. In an alternative method, the aluminum alkyl such as aluminum trimethyl can be desirably contacted with a hydrated salt such as hydrated copper sulfate.

Preferably, the alumoxane is prepared in the presence of a hydrated copper sulfate. The method comprises treating a dilute solution of aluminum trimethyl in, for example, toluene, with copper sulfate represented by the general formula $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The ratio of copper sulfate to aluminum trimethyl is desirably about 1 mole of copper sulfate for 4 to 5 moles of aluminum trimethyl. The reaction is evidenced by the evolution of methane.

The new metallocene compounds usefully employed in accordance with this invention are the mono, bi and tricyclopentadienyl or substituted cyclopentadienyl metal compounds. The metallocenes are represented by the general formula



or a derivative thereof as specified above.

Exemplary hydrocarbyl radicals are methyl, ethyl, propyl, butyl, amyl, isoamyl, hexo, isobutyl, heptyl, octyl, nonyl, dicyl, cetyl, 2-ethylhexyl and phenyl.

Exemplary alkylene radicals are methylene, ethylene and propylene.

Exemplary halogen atoms include chlorine, bromine and iodine and of these halogen atoms, chlorine is preferred.

Exemplary of the alkylidene radicals is methylidene, ethylidene and propylidene.

Of the metallocenes, zirconocenes and titanocenes are most preferred. Illustrative but non-limiting examples of these metallocenes which can be usefully employed in accordance with this invention are monocyclopentadienyl titanocenes such as pentamethylcyclopentadienyl titanium trichloride; substituted bis(Cp)Ti(IV) compounds such as bis(indenyl)Ti diphenyl or dichloride, bis(methylcyclopentadienyl)Ti diphenyl or dihalides and other dihalide complexes; dialkyl, trialkyl, tetra-alkyl and penta-alkyl cyclopentadienyl titanium compounds such as bis(1,2 - dimethylcyclopentadienyl)Ti diphenyl or dichloride, bis(1,2 - diethylcyclopentadienyl)Ti diphenyl or dichloride and other dihalide complexes; silicone, phosphine, amine or carbon bridged cyclopentadiene complexes, such as dimethyl silyldicyclopentadienyl titanium diphenyl or dichloride, methyl phosphine dicyclopentadienyl titanium diphenyl or dichloride, methylene-dicyclopentadienyl titanium diphenyl or dichloride, ethylene bis (4,5,6,7 - tetrahydroindenyl)titanium dichloride and other dihalide complexes.

Illustrative but non-limiting examples of the zirconocenes which can be usefully employed in accordance with this invention are pentamethylcyclopentadienyl zirconium trichloride, the alkyl substituted cyclopentadienes, such as bis(ethyl cyclopentadienyl)zirconium dimethyl, bis(β - phenylpropylcyclopentadienyl)zirconium dimethyl, bis(methylcyclopentadienyl)zirconium dimethyl, and dihalide complexes of the above; di-alkyl, tri-alkyl, tetra-alkyl, and penta-alkyl cyclopentadienes, such as bis(tetramethylcyclopentadienyl)zirconium dimethyl, bis(pentamethylcyclopentadienyl)zirconium dimethyl, bis(1,2 - dimethylcyclopentadienyl)zirconium dimethyl, bis(1,3 - diethylcyclopentadienyl)zirconium dimethyl and dihalide complexes of the above; silicone, phosphorus, and carbon bridged cyclopentadiene complexes such as dimethylsilyldicyclopentadienyl zirconium dimethyl or dihalide and methylphosphine dicyclopentadienyl zirconium dimethyl or dihalide, and methylene dicyclopentadienyl zirconium dimethyl or dihalide.

The ratio of aluminum in the alumoxane to total metal in the metallocene or carbene can be in the range of 0.5:1 to 10,000:1, and preferably 5:1 to 1000:1.

The solvents used in the preparation of the catalyst system are inert hydrocarbons, in particular a hydrocarbon that is inert with respect to the catalyst system. Such solvents are well known and include, for example, isobutane, butane, pentane, hexane, heptane, octane, cyclohexane, methylcyclohexane, toluene and xylene.

As a further control and refinement of polymer molecular weight, one can vary the concentration alumoxane. Higher concentrations of alumoxane in the catalyst system results in higher polymer product molecular weight.

Since, in accordance with this invention, one can produce high viscosity polymer product at relatively high temperature, temperature does not constitute a limiting parameter as with the prior art metallocene/alumoxane catalyst. The catalyst systems described herein, therefore, are suitable for the polymerization of olefins in solution, slurry or gas phase polymerizations and over a wide range of temperatures and pressures. For example, such temperatures may be in the range of -60°C to 280°C and especially in the range of 50°C to 160°C . The pressures employed in the process of the present invention are those well known for, for example, in the range of about 1 to about 500 atmospheres (99.3 to 49644 kPa) and greater.

In a solution phase polymerization the alumoxane is preferably dissolved in a suitable solvent, typically in inert hydrocarbon solvent such as toluene and xylene in molar ratios of about $5 \times 10^{-3}\text{M}$. However greater or lesser amounts can be used.

The soluble metallocenes can be converted to supported heterogeneous catalysts by depositing said metallocenes on typical catalyst supports such as, for example, silica, alumina, and polyethylene. The solid catalysts in combination with an alumoxane can be usefully employed in slurry and gas phase olefin polymerizations.

After polymerization and deactivation of the catalyst, the product polymer can be recovered by

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processes well known in the art for removal of deactivated catalysts and solution. The solvents may be flashed off from the polymer solution and the polymer obtained extruded into water and cut into pellets or other suitable comminuted shapes. Pigments, antioxidants and other additives, as is known in the art, may be added to the polymer.

5 The polymer product obtained in accordance with this invention will have a weight average molecular weight in the range of 1,400,000 to 500 and preferably 500,000 to 1000.

The polydispersities (molecular weight distribution) expressed as M_w/M_n are typically from 1.5 to 4.0. The polymers contain 1.0 chain end unsaturation per molecule. Broadened MW can be obtained by employing two or more of the metal cyclopentadienyls in combination with the alumoxane as described in
10 cofil application entitled Process and Catalyst for Producing Polyethylene having a Broad Molecular Weight Distribution (EP—A—128 045).

The polymers produced by the process of this present invention are capable of being fabricated into a wide variety of articles, as is known for homopolymers of ethylene and copolymers of ethylene and higher
15 alpha-olefins. The present invention is illustrated by the following examples.

Examples

In the examples following the molecular weights were determined on a Water's Associates Model No. 150C GPC (Gel Permeation Chromatography). The measurements were made by dissolving polymer
20 samples in hot trichlorobenzene (TCB) and filtered. The GPC runs were performed at 145°C in TCB at 1.5 ml/min using two Shodex A80 M/S Gel columns of 9.4 mm internal diameter from Perkin Elmer Inc. 300 milliliter of 3.1 percent solutions in TCB were injected and the chromatographic runs monitored at sensitivity equal -64 and scale factor equal 65. The samples were run in duplicate. The integration parameters were obtained with a Water's Associates data module. An antioxidant, N - phenyl - 2 -
25 naphthylamine, was added to all samples.

In the examples following the alumoxane was prepared in the following manner:
600 cm³ of a 14.5% solution of triethylaluminum (TEAL) in heptane was added in 30 cm³ increments
at 5 minute intervals, with rapid stirring, to 200 cm³ toluene in a Zipperclave reactor under nitrogen and
maintained at 100°C. Each increment was immediately followed by the addition of 0.3 cm³ water. The
30 reactor was vented of methane after each addition. Upon completion of the addition, the reactor was stirred for 6 hours while maintaining the temperature at 100°C. The mixture, containing soluble alumoxane and a small quantity of insoluble alumina, is allowed to cool to room temperature and settle. The clear solution containing the soluble alumoxane is separated by decantation from the solids.

The molecular weights were determined by gel permeation chromatography at 145°C on a Waters GPC
35 150C.

Example 1 (comparative)

A 1-liter stainless steel pressure vessel, equipped with an incline blade stirrer, an external water jacket for temperature control, a septum inlet and vent line, and a regulated supply of dry ethylene and nitrogen,
40 was dried and deoxygenated with a nitrogen flow. 500 cm³ of dry, degassed toluene was introduced directly into the pressure vessel. 10.0 cm³ of 0.785 molar (in total aluminum) alumoxane was injected into the vessel by a gas tight syringe through the septum inlet and the mixture was stirred at 1,200 rpms and
80°C for 5 minutes at 0 psig (99.3 kPa) of nitrogen. 0.091 mg bis(cyclopentadienyl) zirconium dichloride dissolved in 2.0 ml of dry, distilled toluene was injected through the septum inlet into the vessel. After 1
45 minute, ethylene at 60 psig (515 kPa) was admitted and while the reaction vessel was maintained at 80°C. The ethylene was passed into the vessel for 30 minutes at which time the reaction was stopped by rapidly venting and cooling. 13.6 g of powdery white polyethylene having a M_n of 39,500 and a M_w of 140,000 with a molecular weight distribution of 3.5.

Example 2

A 1-liter stainless steel pressure vessel, equipped with an incline blade stirrer, an external water jacket for temperature control, a septum inlet and vent line, and a regulated supply of dry ethylene and nitrogen,
was dried and deoxygenated with a nitrogen flow. 400 cm³ of dry, degassed toluene was introduced directly into the pressure vessel. 20.0 cm³ of alumoxane (.785 mmoles in total aluminum) was injected into
55 the vessel by a gas tight syringe through the septum inlet and the mixture was stirred at 1,200 rpms and 80°C for 5 minutes at 0 psig (99.3 kPa) of nitrogen. 0.2101 mg bis(methylcyclopentadienyl) zirconium dichloride dissolved in 2.0 ml of dry, distilled toluene was injected through the septum inlet into the vessel to give an Al/Zr ratio of 24×10^3 . After 1 minute, ethylene at 60 psig was admitted for 30 minutes while maintaining the reaction vessel at 80°C. The reaction was stopped by rapidly venting and cooling. 28.6 g of
60 powdery white polyethylene having a M_n of 55,900 and a M_w of 212,000 with a molecular weight distribution of 3.8 and activity (kg/g.h.atm) of 467.

Example 3—5

Examples 3—5 were performed as Example 2 except that the metallocenes listed in Table I were
65 substituted for the metallocene in Example 2. The results of the examples are summarized in Table I.

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Examples 6—8

Examples 6—8 were performed as Example II except that 0.2 mg of metallocenes as listed in Table II and 9.0 cm³ alumoxane were employed giving an Al/Zr of 8×10³. The results are summarized in Table II.

TABLE I
Substituted cyclopentadiene (Cp) ligand effects

| Example | Catalyst ^a | \bar{M}_w | \bar{M}_n | MWD | Activity kg/g.h.atm |
|---------|---|-------------|-------------|-----|------------------------|
| 1 | Cp ₂ ZrCl ₂ | 140,000 | 39,500 | 3.5 | 252 |
| 2 | (MeCp) ₂ ZrCl ₂ | 212,000 | 55,900 | 3.8 | 467 |
| 3 | (EtCp) ₂ ZrCl ₂ | 171,000 | 44,700 | 3.8 | 306 |
| 4 | (B-PP-Cp) ₂ ZrCl ₂ ^b | 282,000 | 78,200 | 3.6 | 335 |
| 5 | (Me ₅ Cp) ₂ ZrCl ₂ | 63,000 | 13,200 | 4.7 | 71 |

^aAl/Zr=24,000

^bpp=phenyl propyl

TABLE II

| Example | Catalyst ^a | \bar{M}_w | \bar{M}_n | MWD | Activity kg/g.h.atm |
|---------|---|-------------|-------------|-----|------------------------|
| 6 | (Me ₅ Cp) ₂ ZrCl ₂ | 47,300 | 13,200 | 3.6 | 142 |
| 7 | (MeCp) ₂ ZrCl ₂ | 180,000 | 48,300 | 3.7 | 278 |
| 8 | (EtCp) ₂ ZrCl ₂ | 184,000 | 50,000 | 3.7 | 281 |

^aAl/Zr=8,000

The physical properties of a polyethylene are largely determined by the polymer molecular weight and the polymer density. The previous examples have demonstrated that through the ligand effect, one can control the molecular weight of polyethylenes. The following examples demonstrate that through the same ligand effects, one can control the polymer density in copolymers such as ethylene copolymers. In addition, the control of polymer density in the following examples is demonstrated at fixed reaction conditions indicating that density control is mediated by ligand effects on the catalyst reactivity ratios.

Example 9 (comparative)

A 1-liter stainless steel pressure vessel, equipped with an incline blade stirrer, an external water jacket for temperature control, a septum inlet and vent line, and a regulated supply of dry ethylene and nitrogen, was dried and deoxygenated with a nitrogen flow. 400 cm³ of dry, degassed toluene was introduced directly into the pressure vessel. 10.0 cm³ of alumoxane solution (0.8 moles in total aluminum) was injected into the vessel by a gas tight syringe through the septum inlet and the mixture was stirred at 1,200 rpm and 50°C for 5 minutes at 0 psig (99.3 kPa) of nitrogen. 200 cm³ of liquid propylene at 25°C was then added resulting in a pressure of 126.2 psig. (969.4 kPa) 0.113 mg of bis(cyclopentadienyl)zirconium dimethyl in 10 ml of toluene was injected through the septum inlet into the vessel. Ethylene at 152.1 psig (1148 kPa) was admitted and the reaction vessel was maintained at 50°C. The ethylene was passed into the vessel for 30 minutes at which time the reaction was stopped by rapidly venting and cooling the reactor. 66.0 g of copolymer having an intrinsic viscosity of 0.74 was isolated which contained 31 mole % propylene. The density was 0.854 g/cm³ at 23°C.

Example 10

A 1-liter stainless steel pressure vessel, equipped with an incline blade stirrer, an external water jacket for temperature control, a septum inlet and vent line, and a regulated supply of dry ethylene and nitrogen, was dried and deoxygenated with a nitrogen flow. 400 cm³ of dry, degassed toluene was introduced directly into the pressure vessel. 10.0 cm³ of alumoxane solution (0.8 moles in total aluminum) was injected into the vessel by a gas tight syringe through the septum inlet and the mixture was stirred at 1,200 rpm

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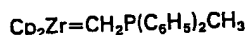
and 50°C for 5 minutes at 0 psig of nitrogen. 200 cm³ of liquid propylene at 25°C was then added resulting in a pressure of 126.2 psig. (969.4 kPa) 0.102 mg of dimethylsilyl - cyclopentadienyl zirconium chloride in 10 ml of toluene was injected through the septum inlet into the vessel. Ethylene at 152.4 psig (1150 kPa) was admitted and the reaction vessel was maintained at 50°C. The ethylene was passed into the vessel for 30 minutes at which time the reaction was stopped by rapidly venting and cooling the reactor. 12.0 gms of copolymer having an intrinsic viscosity of 0.52 was isolated which contained 43 mole % propylene. The density was 0.854 g/cm³ at 23°C.

Example 11

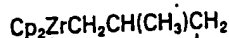
A 1-liter stainless steel pressure vessel, equipped with an incline blade stirrer, an external water jacket for temperature control, a septum inlet and vent line, and a regulated supply of dry ethylene and nitrogen, was dried and deoxygenated with a nitrogen flow. 400 cm³ of dry, degassed toluene was introduced directly into the pressure vessel. 10.0 cm³ of alumoxane solution (0.8 moles in total aluminum) was injected into the vessel by a gas tight syringe through the septum inlet and the mixture was stirred at 1,200 rpm and 50°C for 5 minutes at 0 psig (99.3 kPa) of nitrogen. 200 cm³ of liquid propylene at 25°C was then added resulting in a pressure of 126.2 psig (969.4 kPa) 0.417 mg of bis(pentamethylcyclopentadienyl)zirconium dimethyl in 10 ml of toluene was injected through the septum inlet into the vessel. Ethylene at 151.5 psig (1140 kPa) was admitted and the reaction vessel was maintained at 50°C. The ethylene was passed into the vessel for 25 minutes at which time the reaction was stopped by rapidly venting and cooling the reactor. 30.5 g of copolymer having an intrinsic viscosity of 0.81 was isolated which contained 3.6 mole % propylene. The density was 0.934 g/cm³ at 23°C.

Claims

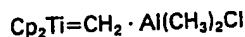
1. A catalyst suitable for the polymerisation of an olefin comprising (a) the carbene represented by the formula



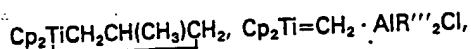
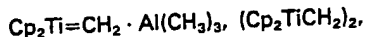
and its derivative of the formula



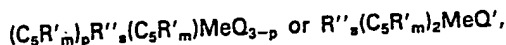
and the carbene represented by the formula



and the derivatives of this carbene



wherein Cp is a cyclopentadienyl or substituted cyclopentadienyl radical, and R''' is an alkyl, aryl or alkylaryl radical having from 1—18 carbon atoms; or a compound of the formula



wherein Me is a Group 4b, 5b or 6b metal, (C₅R'_m) is cyclopentadienyl or substituted cyclopentadienyl, each R' which can be of the same or different, is hydrogen, an alkyl, alkenyl, aryl, alkylaryl or arylalkyl radical having from 1 to 20 carbon atoms or two R' substituents together form a fused C₄—C₆ ring, R'' is a C₁—C₄ alkylene radical, a dialkyl germanium or silicone or an alkyl phosphine or amine radical bridging two (C₅R'_m) rings, each Q which can be the same or different, is aryl, alkyl, alkenyl, alkylaryl or arylalkyl radical having from 1 to 20 carbon atoms or halogen, Q' is an alkylidene radical having from 1 to 20 carbon atoms, s is 0 or 1, p is 0, 1 or 2; provided that s is 0 when p is 0; m is 4 when s is 1; m is 5 when s is 0; and that at least one R' is a hydrocarbyl radical when s=0 and Q is an alkyl radical or halogen and (b) an alumoxane.

2. A catalyst according to claim 1 wherein when p is 0, Q is chlorine and R' is methyl, ethyl or butyl.

3. A catalyst according to claim 1 wherein compound (a) is bis(cyclopentadienyl) titanium diphenyl, bis(cyclopentadienyl) Ti=CH₂Al(CH₃)₂Cl, bis(methylcyclopentadienyl) zirconium dichloride, bis(ethylcyclopentadienyl) zirconium dichloride, bis(β-phenylpropylcyclopentadienyl) zirconium dichloride, bis(pentamethylcyclopentadienyl) zirconium dichloride, bis(tetramethylcyclopentadienyl) zirconium dimethyl, bis(ethylcyclopentadienyl) zirconium dimethyl or ethylene bis(4,5,6,7-tetrahydroindenyl) titanium dichloride.

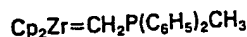
4. A process for polymerising one or more olefins which comprises conducting the polymerisation in the presence of a catalyst system as claimed in any one of claims 1 to 3.

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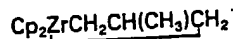
5. A process according to claim 4 wherein the olefin is ethylene or an alpha-olefin having from 3 to 8 carbon atoms per molecule.

Patentansprüche

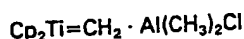
1. Katalysator, geeignet für die Polymerisation eines Olefins, enthaltend (a) das Carben der Formel



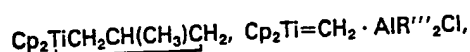
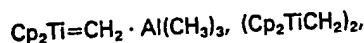
und sein Derivat der Formel



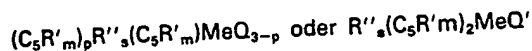
und das Carben der Formel



und die Derivate dieses Carbens



worin Cp ein Cyclopentadienyl oder ein substituierter Cyclopentadienylrest ist und R''' ein Alkyl-, Aryl- oder Alkylarylrest mit 1 bis 18 Kohlenstoffatomen ist; oder eine Verbindung der Formel



ist, worin Me ein Metall der Gruppe 4b, 5b oder 6b ist, (C₅R'_m) ein Cyclopentadienyl- oder ein substituierter Cyclopentadienylrest ist, jeder Rest R', der gleich oder verschieden sein kann, ein Wasserstoff-, ein Alkyl-, Alkenyl-, Aryl-, Alkylaryl- oder Arylalkylrest mit 1 bis 20 Kohlenstoffatomen ist oder zwei R'-Substituenten zusammen einen kondensierten C₄-C₆-Ring bilden, R'' ein C₁-C₄ Alkylrest, ein Dialkylgermanium oder Silicon oder ein Alkylphosphin oder Aminrest, der zwei (C₅R'_m) Ringe miteinander verbindet, ist, jeder Rest Q, der gleich oder verschieden sein kann, ein Aryl-, Alkyl-, Alkenyl-, Alkylaryl- oder Arylalkylrest mit 1 bis 20 Kohlenstoffatomen oder ein Halogenatom ist, Q' ein Alkylidenrest mit 1 bis 20 Kohlenstoffatomen ist, s 0 oder 1 ist, p 0, 1 oder 2 ist; mit der Maßgabe, daß s 0 ist, wenn p 0 ist; m 4 ist, wenn s 1 ist; m 5 ist, wenn s 0 ist und daß mindestens ein Rest R' ein Hydrocarbylrest ist, wenn s=0 und Q ein Alkylrest oder Halogenatom ist und (b) ein Alumoxan.

2. Katalysator nach Anspruch 1, worin, wenn p 0 ist Q Chlor und R' Methyl, Ethyl oder Butyl ist.

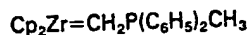
3. Katalysator nach Anspruch 1, worin die Verbindung (a) bis(Cyclopentadienyl) - Titandiphenyl, bis(Cyclopentadienyl) - Ti=CH₂Al(CH₃) bis(Methylcyclopentadienyl) - Zirkoniumdichlorid, bis(Ethylcyclopentadienyl) - Zirkoniumdichlorid, bis(β - Phenylpropylcyclopentadienyl) - Zirkoniumdichlorid, bis(Pentamethylcyclopentadienyl) - Zirkoniumdichlorid, bis(Tetramethyl - cyclopentadienyl) - Zirkoniumdimethyl, bis(Ethylcyclopentadienyl) - Zirkoniumdimethyl oder Ethylen bis(4,5,6,7 - Tetrahydroindenyl) - Titandichlorid ist.

4. Verfahren zur Polymerisation eines oder mehrerer Olefine, bei dem man die Polymerisation in Gegenwart eines Katalysatorsystems nach einem der Ansprüche 1 bis 3 durchführt.

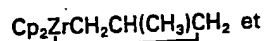
5. Verfahren nach Anspruch 4, bei dem das Olefin Ethylen oder ein alpha-Olefin mit 3 bis 8 Kohlenstoffatomen pro Molekül ist.

Revendications

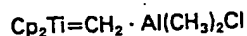
1. Catalyseur apte à être utilisé pour la polymérisation d'une oléfine, comprenant (a) le carbène représenté par la formule



et son dérivé de formule

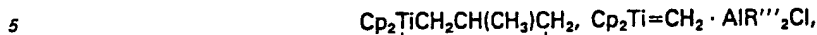


le carbène représenté par la formule



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et les dérivés de ce carbène,



où Cp est un radical cyclopentadiényle ou cyclopentadiényle substitué, et R''' est un radical alkyle, aryle ou alkylaryle ayant 1 à 18 atomes de carbone; ou un composé de formule



dans laquelle Me est un métal du Groupe 4b, 5b et 6b, (C₅R'_m) est un radical cyclopentadiényle ou cyclopentadiényle substitué, chacun des R' qui peuvent être identiques ou différents représente l'hydrogène, un radical alkyle, alcényle, aryle, alkylaryle ou arylalkyle ayant 1 à 20 atomes de carbone ou bien deux substituants R' forment ensemble un noyau condensé en C₄ à C₆, R'' est un radical alkylène en C₁ à C₄, un dialkylgermanium ou une silicone ou un radical alkylphosphine ou amine pontant deux noyaux (C₅R'_m), chacun des Q qui peuvent être identiques ou différents est un radical aryle, alkyle, alcényle, alkylaryle ou arylalkyle ayant 1 à 20 atomes de carbone ou un halogène, Q' est un radical alkylidène ayant 1 à 20 atomes de carbone, s a la valeur 0 ou 1, p a la valeur 0, 1 ou 2; sous réserve que s soit égal à 0 lorsque p est égal à 0; que m soit égal à 4 lorsque s est égal à 1; que m soit égal à 5 lorsque s est égal à 0; et qu'au moins l'un des R' soit un radical hydrocarbyle lorsque s est égal à 0 et Q est un radical alkyle ou un halogène, et (b) un alumoxane.

2. Catalyseur suivant la revendication 1, dans lequel p est égal à 0, Q est le chlore et R' est un radical méthyle, éthyle ou butyle.

25 3. Catalyseur suivant la revendication 1, dans lequel le composé (a) est le bis(cyclopentadiényl)titane-diphényle, le bis(cyclopentadiényl)Ti=CH₂Al(CH₃)₂Cl, le dichlorure le bis(méthylcyclopentadiényl)-zirconium, le dichlorure de bis(éthylcyclopentadiényl)zirconium, le dichlorure de bis(β - phénylpropylcyclopentadiényl)zirconium, le dichlorure de bis(pentaméthylcyclopentadiényl)zirconium, le bis(tétraméthylcyclopentadiényl)zirconium - diméthyle, le bis(éthylcyclopentadiényl)zirconium - diméthyle ou le dichlorure d'éthylène - bis(4,5,6,7 - tétrahydro - indényl)titane.

4. Procédé de polymérisation d'une ou plusieurs oléfines, qui consiste à conduire la polymérisation en présence d'un catalyseur suivant l'une quelconque des revendications 1 à 3.

5. Procédé suivant la revendication 4, dans lequel l'oléfine est l'éthylène ou une alpha-oléfine ayant 3 à 8 atomes de carbone par molécule.